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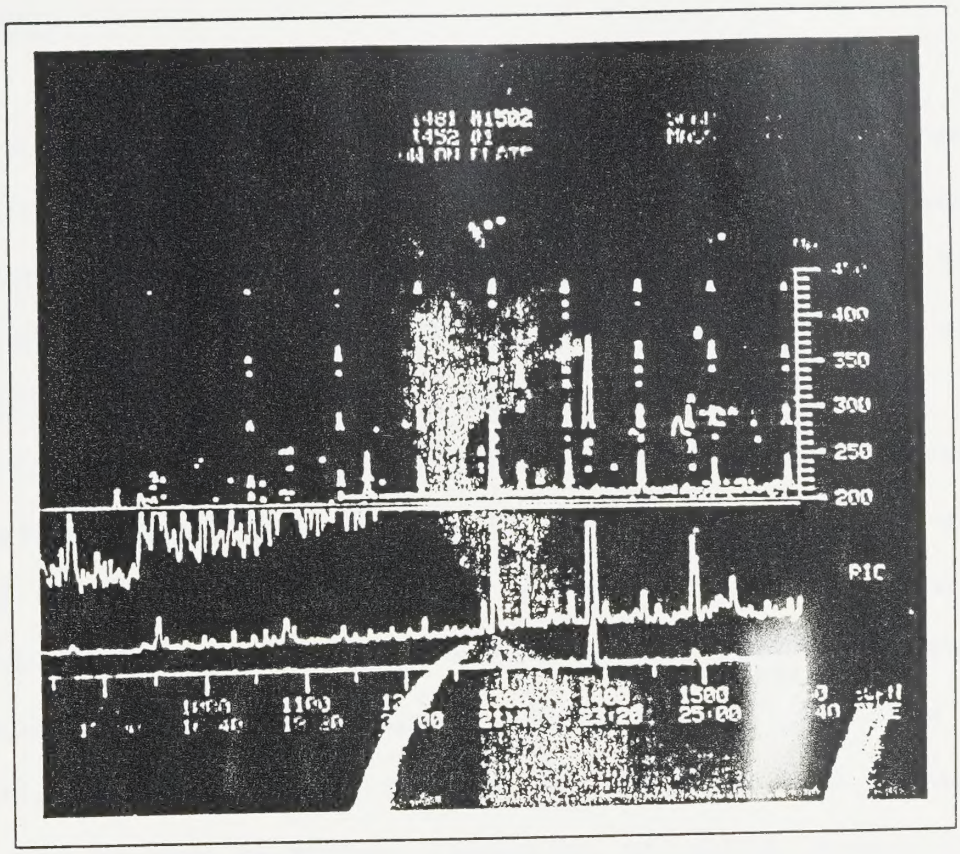

CHEMICAL ANALYSIS OF PRE AND POST FLARE GASES

SUBMITTED TO

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UPPER OTTAWA STREET LANDFILL STUDY

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Summary

A gas recovery and flaring study was undertaken to determine the feasability of burning the landfill gas at the Upper Ottawa Street Landfill Site. The first study determined that the gas must be diluted with air in order to achieve an efficient flare. The ratio of 10:1 (air:landfill gas) was determined as the optimum mixture. A maximum flame temperature of 950°C was recorded under these conditions. Combustion efficiency of organics and chlorinated organics was measured at greater than 90 percent for most compounds. Benzene, naphthalene and benzofuran have lower combustion efficiencies, however this may be due to actual formation of these compounds in the flame. Incomplete oxidation of alkyl aromatics resulted in increased levels of styrene, benzaldehyde and methyl benzaldehyde. Nitromethane was produced in significant quantities.

Introduction

This work is the second part of the study to determine the feasibility of burning landfill gas at the Upper Ottawa Street Landfill Site. The work was requested by Anne Koven, Research Director, of the Upper Ottawa Street Landfill Committee.

The first flaring study determined several important parameters. The composition of the undiluted landfill gas was determined to be approximately 50% methane, 35% carbon dioxide, 10% nitrogen and 3% oxygen. Theoretically this concentration of hydrocarbon supports combustion and the pilot flare apparatus proved this experimentally, although the flame was poor.

Analysis of the pre and post flare gases during the first study indicated that combustion was not complete. High concentrations of methane were detected in the post flare gas samples. The flame extended up to 50 feet above the chimney. The conclusions from the first study were that combustion was incomplete due to an overly fuel rich flame. It was obvious that in order to burn the landfill gases efficiently, it was necessary to introduce oxygen into the system so that the minimum oxygen to methane ratio was 2:1 according to the balanced equation 1:

$$CH_4 + 2O_2 - CO_2 + 2H_2O \qquad \text{(eq. 1)}$$

The flaring apparatus was modified by Connestoga-Rovers Associates to allow dilution of the landfill gas (LFG) by ambient air. The minimum air:LFG ratio required to satisfy eq. 1 was 5:1. The chimney was also extended in order to contain the flame, and provide better sampling.

In this, the second part of the flaring study, the first day was spent determining the air:LFG ratio that would optimize combustion efficiency of the volatile organics, including methane. Three ratios of air:LFG were set up at 5:1, 7:1 and 11:1. The temperatures at various heights in the chimney were recorded at each ratio setting, and the results, as obtained by Conestoga-Rovers are listed in Table 1. Post combustion gases were collected at each setting and were analysed for constituent gases. The results of the analysis indicated a slightly higher level of residual methane in the 5:1 sample than the 11:1 sample. This fact, plus the higher temperatures recorded at the :1 setting led us to choose 10:1 as the ratio of air:LFG up which we would perform more extensive sampling and analysis.

On the second day, pre and post combustion samples were taken in gas bags, tenax sorbent tubes and gas cylinders pressurized to 90 psi. The temperatures were measured at 10:1 amd 20:1 and are listed in Table 1.

The objectives of sample analysis for trace organics in the second study were to determine (a) the degree of destruction of LFG organics by the flame, and (b) whether any toxic or hazardous compounds were being formed in the flame.

Methods and Analysis

A teflon oil-less vacuum/compressor pump was used to draw gases through the tenax sorbent tubes and to fill the gas bags and cylinders. A twenty foot length of 1/4 inch copper tubing was used to sample the hot gases in the chimney. The sorbent tubes were placed in-line before the pump, and the bags and cylinders after the pump for sampling.

The tenax sorbent tubes were thermally desorbed in the Unacon 780B Concentrator (Envirochem) equipped with a 30M DB-1 fused silica capillary column. The total ion current chromatograms are included in Appendix A. The eluants were analysed by mass spectrometry on a Finnigar 4500 equipped with the Incos data system. All EI spectra were obtained at 70 eV.

A Hewlett-Packard 5700 GC/ECD was used to screen the gas samples for halogenated compounds using Poropak Q and OV-1 columns.

An Antek GC/TCD with a sampling loop was used to quantify the concentrations of CH_4, O_2, N_2 and CO_2 using Molecular Sieve 5A and Carbosieve B columns.

A Hewlett-Packard 5840 equipped with automatic valves and several columns, specially designed for gas analysis, was used to screen for the C_1-C_3 hydrocarbons.

Comment on Thermal Desorption Mass Spectrometry (TDMS)

The analysis of organics in air is not a new science. Industrial Hygienists conduct many such studies as a daily routine and have very specific methodology. Fortunately they know what substances to monitor prior to analysis.

Such is not the case for the Upper Ottawa Street Landfill Gas Flaring Study. Our work to date has been a valuable guide as to the kinds of volatile compounds that one might expect in the gas leading to the flame. Very little could be predicted as to the composition of the post flare gas.

Thermal desorption mass spectrometry was recommended as a viable technique[1,2,3] although its shortcomings were understood. For example, highly volatile compounds could not be quantitatively retained on solid sorbents if the sampling volume was very high; while non-volatile compounds, such as benzo (a) pyrene, which exist in the atmosphere at concentrations lower than volatile compounds, generally could not be detected analytically without very high sampling volumes. This study used relatively low sample volumes and

thus PAH compounds are unlikely to be found. Another problem is that reactive compounds, such as styrene and ethylene oxide, which tend to polymerize on active surfaces, were more effectively retained on sorbents which had relatively more active surfaces. These paradoxes indicate areas where compromises would be required to obtain a single sampling system. Our professional judgement indicated that the selection of tenax/ambersorb/charcoal and a DB-1-Capillary column system would analyse the range of compounds deemed necessary for this phase of study.

Results

The gas bag and cylinder samples were used to analyse for the constituent gases via GC/TCD, GC/ECD and GC/FID. These results are listed in Table II. The combustion efficiency for methane and 1,1,1 trichloroethane is greater than 95%. There does, however, appear to be an increase in the C-2 hydrocarbons after burning.

The results of the sorbent tube analysis by GC/MS are listed in Table III, which lists only those compounds detected in relatively high concentration in the post combustion gases. The concentrations listed are approximate due to the terms of reference of this study and the variability of the sorbent tube method. The absolute values, based on the response of toluene, are not as meaningful as

the relative concentrations. The combustion efficiency of toluene, ethyl benzene, xylenes, C_3-benzenes, C_4 benzenes, indenes and dichlorobenzene is greater than 90%. The combustion efficiency of benzene, benzofuran, and naphthalene is less than 90%, while styrene, nitromethane, benzaldehyde and methyl benzaldehyde all increase in concentration. The presence of nitromethane is based on the EPA/NIH library and has been confirmed. Dimethylnitrosamine was not detected in either the pre or post combustion samples. The sorbent tube method would detect dimethylnitrosamine if it were present above 50 ppb. The concentration of alkyl hydrocarbons, alcohols, aldehydes and ketones dropped dramatic lly in the post flare samples, with greater than 90% combustion efficiency.

TABLE 1

TEMPERATURE PROBE READINGS (^{O}C)

DIFFERENT AIR TO LFG RATIOS

	Day 1			Day 2	
Ratio	4:1	7:1	11:1	10:1	20:1
Top Port	300	N/A	N/A	430	380
Port #9	N/A	N/A	N/A	N/A	N/A
Port #8	530	N/A	N/A	N/A	N/A
Port #7	520	510	N/A	N/A	N/A
Port #6	590	540	N/A	470	440
Port #5	600	590	390	500	440
Port #4	650	730	490	560	470
Port #3	650	820	530	620	550
Port #2	810	810	690	710	640
Port #1	720	875	910	950	970

TABLE II

CONCENTRATION OF COMPONENTS

IN LFG* AND FLARE GASES

	LFG (UNDILUTED)	LFG:AIR (10:1) (FLAME OFF)	LFG:AIR(10:1) (FLAME ON)
N_2	10.3%	73.6%	75.6%
O_2	2.9%	19.8%	12.6%
CH_4	51.4%	4.1%	0.2%
CO_2	34.0%	2.5%	7.0%
THC	0.4%	0.03%	0.02%
Ethane	T	1 ppm	T
Ethene	21.6 ppm	4 ppm	9.7 ppm
Acetylene	T	0.6 ppm	1.4 ppm
Propane	-	-	-
1,1,1-trichloroethane	17.1 ppm	2.2 ppm	0.05 ppm
Dichloroethene	T	T	ND
Tetrachloroethene	0.2 ppm	T	ND

*LFG - Land Fill Gas

TABLE III

Approximate Concentrations of Organics
Trapped on Tenax Sorbent Tubes (PPM)
Relative to the Concentration of Toluene

	Port 5 (1L) Flame Off	Port 5 (1L) Flame On	Port 5 (3L) Flame On	Top of Chimney Flame On (3L)
Furan	30	1	5	8
Sulphur Dioxide	2	5	14	3
Benzene	47	9	8	17
Toluene	102	4	4	11
C_2-Benzenes	88	0.4	0.7	1.7
C_3-Benzenes	43	0.1	0.2	0.4
C_4-Benzenes	6	0	0.1	0
Dihydroindene (C_9H_{10})	10	0.2	0.6	0.5
Indene	1.6	0.1	0.1	0.1
Dichlorobenzene	1.9	0	0	0
Benzofuran	0.4	0.2	0.3	0.2
Benzaldehyde	0	0.4	0.5	0.3
Cl-Benzaldehyde	0	0.2	0.3	0.2
Naphthalene	1.0	0.4	0.8	0.6

Discussion

Flame chemistry is a complex field requiring in-depth study even when the fuel is one of known constituency. The task we have undertaken is an attempt to assess the gross factors involved in mixing and burning an extremely complex gas mixture under less than ideal conditions. This flaring study was not designed as a research project but simply a survey to determine the feasability of collecting and burning landfill gas at the Upper Ottawa Street Site.

It is apparent from the GC/MS data collected that most of the volatile organics are destroyed. A few compounds increase in concentration, however the majority of compounds are oxidized to CO_2. The chlorinated compounds are completely destroyed.

Some compounds increase in amount following combustion and a few compounds were detected in the post-flare sample that were not present in the pre-flare gas. Nitromethane is an example of the latter. It is of some concern for two reasons:

1. It is in high concentrations in comparison to the levels of other constituents.
2. The absolute identification of nitromethane could not be accomplished during the duration of these tests.

The apparently low combustion efficiencies for benzene, naphthalene and benzofuran may actually be due to formation of these compounds in the flame. Table III lists only those compounds detected in relatively high concentration in the post combustion gases. The rise in CO_2 levels after the flame, and elimination of odour by the flame, indicates oxidation of sulphur containing compounds.

Conclusions

The objectives of this study were met successfully. Firstly, the combustion efficiency of the flame is detailed in Tables II and III, and secondly, new compounds formed by the flame were detected and identified. The flame eliminated the foul odour of the gas, thereby, alleviating one of the major irritating aspects of the dump site. Dimethyl-nitrosamine was not detected in either the pre nor post combustion gases. Some compounds formed in the flame may not be detected by the methodology used in this study, however the best methodology available today was used to obtain a broad spectrum of organics.

A toxicological assessment of the combustion products is required before recommending a full scale landfill gas recovery and burning.

References

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3. D.S. West F.N. Hodgson, J.J. Brooks, C.L. Heflin, T.N. Hughes and C.R. McMillin. Portable Miniature Samples For Potential Airborne Carcinogens in Micro-Environments, Phase 2 Evaluation. Monsanto Research Corporation. EPA-600/2-81-165, September 1981.

FIGURE 1

TENAX TUBE FIELD BLANK

FIGURE 2

TENAX TUBE PORT 5

FLAME ON

ONE MINUTE SAMPLE

FIGURE 3

TENAX TUBE PORT 5

FLAME OFF

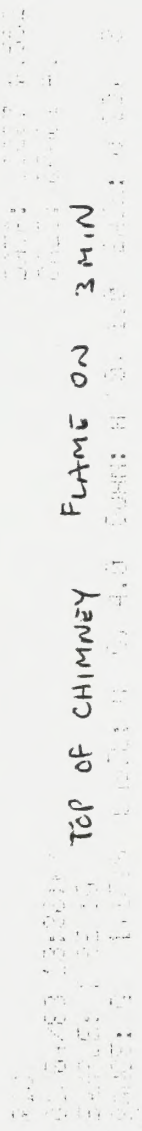
ONE MINUTE SAMPLE

FIGURE 5

TENAX TUBE TOP OF CHIMNEY

FLAME ON

THREE MINUTE SAMPLE



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